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CERTAIN EFFECTS OF PRESSURE ON SEVEN RARE EARTH METALS

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Introduction

The Atomic Energy Commission has recently made available, under the Directorship of Dr. F. H. Spedding at its laboratory in Ames, Iowa, seven new rare earth metals in massive, highly purified, form. The only elements now missing from the fifteen elements of this series, as prepared at Ames, are prometheum, europium, and terbium. The seven metals newly made available are: samarium, dysprosium, holmium, erbium, thullium, ytterbium, and lutecium.

In previous papers[1] I have presented measurements for the effects of pressure on the other five available elements, namely: lanthanum, cerium, praseodymium, neodymium, and gadolinium. The properties studied under pressure were: the volume compression up to 40,000 kg/cm²; the electrical resistance in two pieces of apparatus, in the first to 30,000 kg/cm² under truly hydrostatic pressure, and in the second to 100,000 under a stress only approximately hydrostatic; and the plastic shearing strength as a function of pressure up to 100,000. These measurements were all made at room temperature. In addition, the atmospheric densities, specific resistance, and temperature coefficient of resistance between room

temperature and 0° were determined. In the present paper the same data are presented for the seven metals newly available. In addition, because of its special interest, the electrical resistance of ytterbium has been measured up to 200°, but only to a pressure of 7,000 kg/cm² at the higher temperatures.

The five metals previously measured all showed anomalies under pressure, the anomaly being different for each one of them. The most spectacular of these anomalies was a large discontinuity in the resistance and volume of cerium near 12,000 kg/cm², doubtless due to an electronic transition within the atom. The new metals here investigated also show anomalies, with the sole exception of samarium. The anomalies of five of these six metals are minor. Ytterbium, however, is drastically out of line. Its atmospheric density, melting point, and mechanical softness are much lower than those of its neighbors. Under pressure the compressibility is three times too high, and the electrical resistance is highly anomalous, at first increasing rapidly and at an accelerated rate to the neighborhood of 50,000 kg/cm², where there is a rapid collapse by a factor of the order of 16 to about three-quarters its initial value.

Apparatus and Method

The apparatus was the same as that used previously[2] except for a modification in the method of measuring resistance to 30,000. This modification was devised in connection with other measurements on various alloys, many of which are brittle or difficult for other reasons to fashion into fine wires. The new method utilizes specimens in the form of thin rectangular flakes. Since the method was available, it was used in the present work, although perhaps not necessary. I did not check by actual trial that it was not feasible to fashion the present rare earth metals into wires, as I had done for the five previous, although the physical properties of some of them, particularly lutecium, made it probable that there would have been difficulties.

For the measurements the rectangular flakes were set on edge in a suitable holder, and the terminals, two for current and two for potential, pressed with springs against the *edge* of the flake. The contacts were made with the sharpened edges of pieces of 0.001 inch sheet steel soldered to the springs. Sharp contacts are

necessary in order to prevent error from the geometrical indefiniteness of the region of contact which arises when even the finest feasible wire is used for the contact. In the present work the rectangular flakes had an overall length of roughly 6 mm, and were approximately 1 mm wide and 0.005 cm thick. The current terminals were 4 mm apart and the potential terminals 2 mm apart.

The problem of current flow in a specimen of this shape is capable of formally exact mathematical solution by the method of images. However, because of the logarithmic potentials involved, there are difficulties of convergence when it comes to the numerical computation which I did not overcome. I therefore contented myself with an empirical determination of the correction arising from departure of the lines of current flow from uniform parallelism by dummy experiments on rolled high resistance ribbon, which could be counted on to have the requisite geometrical regularity. The correction thus determined was 1.5%, gratifyingly small. In the following the course was adopted of reducing by 2% the specific resistance calculated on the basis of straight current flow, the difference between 1.5 and 2% being within the error arising from uncertainty in the dimensions.

The sensitiveness of the method is about 1/10,000 on the resistance on absolute resistances of the order of 0.04 ohm.

In the compression measurements to 40,000, pressure was transmitted by an indium sheath, the metals being too hard to use directly.

Detailed Presentation of Data

Samarium. The spectroscopic analysis made at the Ames laboratory gave the following results. Eu, approx. 0.25%; Gd and Nd, less than 0.05%; Ca, weak (i.e. approx. 0.01%); Mg, very weak; Fe, trace; La, Si, and Ta, not detected.

Samarium is rather soft and deforms cold without too much cracking. The density "as received" was 7.45; this increased to 7.50 after exposure to 40,000. The latter may be taken as the best density for the compact metal, there having been no evidence of any permanent irreversible change produced by pressure. For the resistance measurements to 100,000, pieces were cut from the discs sheared in the plastic strength experiments, and used without annealing. The specimen for the resistance measurements to

30,000 was cut from a piece that had been squeezed to a thickness of approximately 0.020 cm between carboloy platens covered with mica at 400° in a stream of helium, allowed to cool with the apparatus, and then filed to 0.007 cm thickness and cut to shape. There was no significant hysteresis in the resistance between increasing and decreasing pressure. The two runs to 100,000 agreed within 4%; the decrements of resistance to 100,000 were increased by a uniform 30% to secure agreement with the results to 30,000 in the common range 20,000 to 30,000.

Results for all the metals, including for convenience of reference the five previously measured, are given in Table I.

Resistance and volume were both smooth functions of pressure, with no episodes or other unusual features. Samarium is the only one of the twelve rare earth metals for which this is the case.
Dysprosium. The spectroscopic analysis by the A. E. C. gave: Y, approx. 0.1%; Ho, less than 0.02%; Ca, Fe, Mg, and Si, weak; Ta, faint trace.

This material was worked to shape for the various resistance measurements by first squeezing between mica-coated carboloy platens heated to 450° in a stream of atmospheric helium and then annealing at a bright red in a stream of helium. The density of the material "as received" was 8.43, which was increased to 8.45 by exposure to 40,000 kg/cm^2.

Three runs were made on the resistance to 30,000; there seems to be a slight pressure seasoning. The tabulated results are those of the third run on a specimen previously exposed to pressure. Two resistance runs were made to 100,000; the decrements of one run had to be reduced by 25% and those of the other by 4% to secure agreement with the measurements to 30,000 in the range 20,000 to 30,000. After this correction the two 100,000 runs were averaged; the maximum adjustment in the averaging process was 1.4% of the total relative resistance at 100,000.

Both high pressure runs agreed in showing a well-developed cusp in the resistance between 70,000 and 80,000, at which the rate of decrease of resistance abruptly increases by a factor of roughly 2. The compression to 40,000 showed no feature.
Holmium. The A. E. C. spectroscopic analysis gave: Er, approx. 0.2%; Dy, approx. 0.1%; Ca and Mg, very weak; Si and Ta, faint trace.

The thermal treatment was the same as for dysprosium. The density, which was initially 8.68, increased to 8.76 after exposure to 40,000.

The compression measurements to 40,000 were smooth, with no suggestion of any anomaly. The resistance measurements, however, make it highly probable that there is a small anomaly somewhere between 20,000 and 40,000, perhaps two. The effect is small and not reproducible in fine detail. Two runs on resistance were made to 30,000. The first, on a specimen not seasoned by a previous application of pressure, but subject to the regular annealing, showed a hysteresis loop of width equal to half the entire pressure effect. The second run, on a specimen seasoned by a previous application of pressure in addition to the annealing, showed diminished hysteresis, but with a possible downward jump at 20,000 of approximately 0.0085 on the proportional resistance.

Three runs were made to 100,000, the first on a not well-annealed specimen and the other two on regularly annealed specimens. These three runs to 100,000 agreed unusually well. All agreed in showing a cusp (downward break in the tangent) between 30,000 and 40,000. In the table the average of the two runs on well-annealed specimens is given. These two runs agreed within 0.5% of the relative resistance at 100,000, and neither run demanded any correction to secure agreement with the measurements to 30,000 in the common range. In the table of final results a cusp is shown between 30,000 and 40,000, and no anomaly at any lower pressure. There is no assurance, however, that this interpretation of the results would survive a more careful investigation.

Erbium. The A. E. C. spectroscopic analysis gave: Y, much less than 0.01%; Ca, very weak; Mg and Si, very faint trace; Dy, Fe, Ho, and La, not detected.

This was received from the A. E. C. in the same batch as the dysprosium and holmium, and was subjected to the same treatment in forming the specimens. The density at room temperature "as received" was 9.05 and after exposure to 40,000, 9.04. The compression measurements were smooth.

Resistance measurements to 30,000 were made on three specimens; only the results of the third have been used in the final results, the first two having been measured before the method was developed into its final form. The three runs agreed within the

TABLE I

Collected Properties of Rare Earth Metals

Pressure Kg/Cm²	La	Ce	Pr	Nd	Sm	Gd	Dy	Ho	Er	Tm	Yb	Lu
Atmospheric Density												
	6.15	6.9	6.5	6.9	7.50	7.96	8.45	8.76	9.04	9.26	7.02	9.81
Specific Resistance at 0° C. and Atmospheric Pressure, × 10^6												
	62.4	76.7	73.7	71.8	88.	140.5 134.5	56.	87.	107.	79.	30.	79.
Temperature Coefficient of Resistance, 0° — Room Temperature												
	.00218	.00087	.00171	.00164	.00148	.00176 .00091	.00119	.00171	.00201	.00195	.00130	.00240
Compression, $\Delta V/V_0$												
5,000	.0194	.0234	.0174	.0152	.0173	.0125	.0130	.0125	.0123	.0128	.0373	.0114
10,000	.0370	.0549 tr	.0329	.0289	.0321	.0242	.0246	.0234	.0229	.0240	.0697	.0224
15,000	.0526	.1655	.0471	.0416	.0459	.0351	.0356	.0351	.0332	.0340	.0978	.0330
20,000	.0665 tr	.1864	.0604	.0536	.0588	.0452	.0456	.0443	.0430	.0439	.1230	.0429
25,000	.0827	.2027	.0729	.0650	.0722	.0545	.0551	.0538	.0525	.0534	.1460	.0523
30,000	.0952	.2154	.0848	.0757	.0824	.0632	.0646	.0626	.0614	.0622	.1657	.0609
35,000	.1072	.2257	.0961	.0858	.0937	.0712	.0731	.0711	.0695	.0706	.1842	.0687
40,000	.1189	.2342	.1069	.0955	.1044	.0785	.0814	.0796	.0775	.0782	.2000	.0760

tr. transition

Effect of Pressure on Resistance, R_p/R_o

Pressure Kg/Cm²	La	Ce	Pr	Nd	Sm	Gd	Dy	Ho	Er	Tm	Yb	Lu
0	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
		tr										
10,000	.9997	.548	.9956	.9850	.9643	.9541	.9765	.978	.973	.9736	1.97	.9869
20,000	.9978	.506	.9959	.9694	.9388	.9115	.9530	.956	.950	.9528	3.88	.9714
	c											
30,000	.9759	.487	.9980	.9600	.9184	.8008	.9295	.934	.932	.9360	7.24	.9525
								c				
40,000	.903	.477	1.0007	.9550	.9047	.7637	.9095	.9095	.9185	.9229	11.13	.9360
									c			
50,000	.867	.469	.9943	.9527	.8951	.7322	.8935	.884	.890	.9128	12.85	.9219
			c									
60,000	.849	.4620	.9312	.9525	.8875	.7056	.8795	.862	.8625	.9042	—	.9097
70,000	.8398	.4625	.8889	.9525	.8817	.6844	.868	.8425	.8435	.8968	.7886	.8991
							c					
80,000	.8362	.4711	.8799	.9544	.8773	.6668	.8475	.827	.8315	.8883	.7696	.8902
90,000	.8368	.4857	.8819	.9572	.8742	.6523	.829	.816	.826	.8794	.7588	.8825
		c										
100,000	.842	.4817	.8902	.9623	.8721	.6405	.8165	.8085	.8235	.8691	.7533	.8761

tr, transition
c, cusp

wider limits of error of the first two. The final run to 30,000 showed definite hysteresis, the width of the loop being about 15% of the entire pressure effect. This hysteresis is disregarded in the final tabulation, which gives the mean with increasing and decreasing pressure in the range to 30,000. The two runs to 100,000 showed a marked cusp, with downward break in the tangent, between 40,000 and 50,000. The decrements of one run had to be decreased by 25% to secure agreement with the 30,000 run; the other run required no correction. The relative resistances at 100,000 given by the two runs differed by 3%; the mean is given in the table.

Although the table represents the resistance as having a cusp, it seems to me highly probable that what we have here is really a first order transition, running with much hysteresis, and so sluggish that equilibrium is not fully attained in a pressure interval 80,000 kg/cm^2 wide. The principal reason for this statement is the unusual behavior of resistance on release of pressure. In general, the resistances obtained with decreasing pressure by this method are of no value in giving good numerical values for the resistance because of the irreversible deformation of the pipestone ring, but nevertheless the measurements were always made as a rough qualitative check. The normal behavior for a material whose resistance decreases with increasing pressure is for the measured resistance to increase on release of pressure, but with wide hysteresis compared with the increasing branch. Both runs with erbium agreed in the highly unusual feature that resistance continued to decrease with release of pressure all the way to nearly 20,000 kg/cm^2, beyond which there was a rapid increase of resistance back toward the initial value. The simplest explanation of this unusual behavior is that the first application of 100,000 has sluggishly produced a new phase, which is irreversibly retained to about 20,000 on release of pressure. This high pressure phase has a positive pressure coefficient of resistance, not the usual sign of the coefficient, but nevertheless one of which there are numerous examples, some of them in the other rare earth metals at high pressures.

Thullium. The A. E. C. spectroscopic analysis gave: Yb and Mg, very weak; Ca, Fe, Si, and Ta, weak. No rare earth other than Yb was detected in the oxide from which the metal was made.

The density "as received" was 9.12, and after exposure to

40,000, 9.26, rather a large increase. The compression measurements were smooth. The resistance specimens, both for the runs to 30,000 and to 100,000, were cut from the discs produced by the shearing experiments, after annealing to a red heat in a stream of helium. The resistance run to 30,000 was smooth and single valued. A second run, terminated at 15,000 by a displaced connection, agreed over the common range with the 30,000 run. Two runs were made to 100,000; the decrements of one had to be reduced by 7% and those of the other by 13% to secure agreement with the 30,000 run over the 20,000 – 30,000 range. At 100,000 the decrement of one run was 10% above the average and that of the other 10% below. In general the results are smooth up to 100,000, but there is a slight anomaly above 80,000, where there is a reversal of curvature with abnormal accelerated decrease of resistance above 80,000. This anomaly was shown by both runs.

Ytterbium. The A. E. C. spectroscopic analysis gave: Ca, very weak; Al and Na, faint trace; Fe, La, Lu, Ta (?) and Tm, not detected.

The properties of this metal are quite out of line with the others of the series, and for this reason more measurements were made on it than usual. Ytterbium is soft mechanically, easily permitting the extreme distortions required to form into wire or to roll to thin sections. However, after such cold working it apparently needs stabilizing, for which an elevation of temperature to 200° is sufficient.

The compression measurements to 40,000 were smooth, with no trace of anomaly. The compression, however, was two and a half to three times larger than to be expected from its position in the series. The density at room temperature "as received" was 6.97, and after exposure to 40,000, 7.02. Something over 9 for the density would be expected from its atomic position.

Resistance measurements to 30,000 were made on rolled material, annealed in helium at 400°. Two runs, one terminated at 23,000 by leak, gave identical results over the common range. The variation of resistance with pressure is a rise at a highly unusually rapid rate with rapidly increasing upward curvature, the increase under 30,000 being by a factor of 7.2. The magnitude of this increase is approached only by strontium, for which the corresponding factor is 3.5. In the range to 30,000 the logarithm of resistance is linear

in pressure to a first approximation. To a second approximation the logarithm is first slightly curved upward, with an inconspicuous inflection near 15,000, followed by slight downward curvature.

Three resistance runs were made to 100,000, two on specimens cut from the shearing disc, used unannealed, and the third on a rolled strip, annealed in helium at 400°. These runs agreed in their qualitative features. The accelerated upward rise of resistance continues beyond 30,000 up to nearly 60,000, where the resistance has increased by a factor of 12 or 13 over its initial value. Here resistance turns abruptly downward, reaching 0.79 of its initial value at 70,000, beyond which it drops smoothly and slightly to 100,000, like a normal metal. The numerical agreement between the three runs was not close, but could all be explained by slight shifts of pressure of the different runs with respect to each other. With curves running as steeply as these, a slight pressure shift may

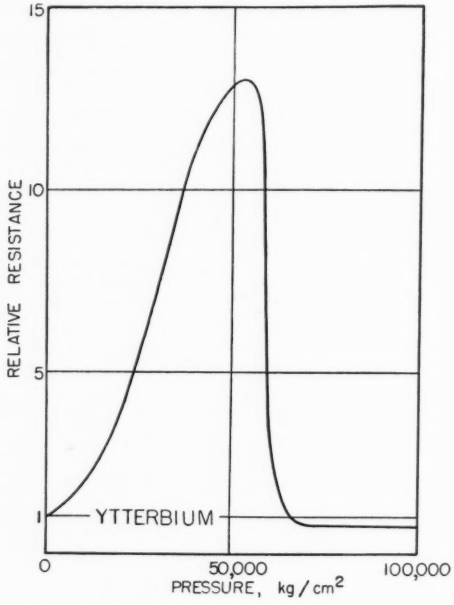

Figure 1. The relative resistance of ytterbium to 100,000 kg/cm².

give wide percentage disagreements, which it is not significant to describe in detail. In one of the runs the large drop of resistance was essentially complete before 60,000, in the second was about half complete at this pressure, and in the third at a slightly higher pressure. The three runs were averaged for the final results. With such large variations the best method of correcting so as to secure agreement with the measurements to 30,000 is to a certain extent a matter of taste. The method adopted was to increase the increments by 30% up to the maximum, and to diminish the absolute resistances beyond 70,000 by 25%. The numerical value for the jump of resistance obtained in this way is doubtless not very good, but the manner of variation in the ranges of slow change should not be greatly in error. The results are shown in Figure 1.

The maximum increase of resistance reached under pressure, by a factor of twelve or thirteen, is so large as to raise the suspicion that this metal may be pushed well toward the semiconducting state by pressure. If so, the question of temperature coefficient becomes important. For this reason additional measurements were made to 200°, in an apparatus designed for other purposes,[3] but available for this, up to a pressure of only 7,000 kg/cm^2, high enough to show the trend. Pressure is transmitted with nitrogen; the apparatus has already been fully described. Since last use the apparatus has been improved by installing a water-cooling cell on the transmitting pipe to prevent heat transfer from the lower cylinder to the upper cylinder in which the manganin pressure gauge is located. In addition, the upper cylinder is cooled with a fan, the net result being that no error is introduced into the manganin gauge readings by possible changes induced by change in temperature of the vessel containing the specimen.

For the measurements to 200° the metal was first squeezed to a rough wire 0.045 inch in diameter by successive passes through the collet of a jeweler's lathe. From 0.045 inch it was rolled cold to a thickness of 0.005 inch. From this rolled strip an elongated dumbbell was cut, the neck of which was 0.075 cm wide and 3.8 cm long. Leads were attached to the enlarged ends of the dumbbell by piercing with a fine needle and threading fine copper wire through the holes and lightly hammering flat. The contact so obtained was not perfect, but sometimes during the course of the measurements had to be restored by current from a small magneto.

Runs were made on initially unannealed material to 7,000 kg/cm² at 0°, 204°, 0°, 101° and 204°. The first increase of temperature to 204° evidently annealed the specimen, because after this run there was a permanent decrease of resistance to 0.85 the initial value. The annealing effect occurred during the rise of temperature at atmospheric pressure before application of pressure, as shown by the fact that the zero was unaltered after the pressure run. The annealing process was apparently completed by the first rise of temperature, because after that the zero had acquired stability as shown by readings of resistance at room temperature and atmospheric pressure between the successive pressure runs. At 0°, the mean pressure coefficient of resistance to 7,000 of the unannealed material given by the first run was about 3 per cent less than that of the annealed material, as given by the third run. In general, the pressure runs with the 7,000 apparatus were entirely satisfactory, the readings being smooth, with no hysteresis, with perfect recovery of zero, and with identical results for the two runs at 204°.

TABLE II

Effect of Pressure on Relative Resistance of Ytterbium at Higher Temperatures

Pressure kg/cm²	0°	R_p/R_{00} 100.6°	203.8°
0	1.000	1.119	1.278
1,000	1.073	1.178	1.336
2,000	1.157	1.245	1.394
3,000	1.244	1.316	1.458
4,000	1.338	1.389	1.529
5,000	1.444	1.471	1.602
6,000	1.558	1.560	1.683
7,000	1.683	1.653	1.766

The relative resistances for the runs to 7,000 are collected in Table II. It will be seen that the suspected reversal of temperature coefficient has occurred at 7,000 between 0° and 100°. The pressure of reversal is evidently a function of temperature, the higher the temperature the higher the pressure.

Lutecium. The A. E. C. spectroscopic analysis gave: Ca and Fe,

weak; Yb, very weak; Mg, Si, and Tm, trace. No other rare earths except Tm and Yb were detected in the oxide from which the metal was made.

The density "as received" was 9.75, and after exposure to 40,000, 9.81. The compression run to 40,000 was made on a specimen formed by cold pressing and not annealed. The resistance measurements over both ranges were made on specimens cut from the discs formed during the shearing experiments and annealed to a bright red in a stream of helium. The compression measurements disclosed no incidents. The resistance was anomalous up to 30,000 in that there is downward curvature, becoming less at the upper end of the range. The two runs to 100,000 showed the same low pressure anomalous curvature; this reverses and becomes normal between 30,000 and 40,000. The decrement of resistance between 20,000 and 100,000 given by the two runs differed by 3.5%. Increase of the average decrement from 20,000 as zero by 12% was necessary to secure agreement with the measurements to 30,000.

Shearing Strength to 100,000 kg/cm^2

Since the significance of the measurements on shearing strength is less definite and more of a relative matter than either compression or resistance, it seems advisable to describe the shearing measurements on all these rare earth metals together, including those on lanthanum, cerium, praseodymium, neodymium and gadolinium, which have not been described in detail previously.

The shearing apparatus is in principle like the steel apparatus formerly used[4] to 50,000 kg/cm^2, but now constructed of carboloy, which permits reaching 100,000 kg/cm^2. Minor alterations are required by the new material. The active surface of shear is a circle 0.25 inches in diameter as before, but now it is the truncated apex of an obtuse cone of 150° double angle, instead of the end of a very short cylindrical boss. The change was necessitated by the shearing off of the edges of the boss which occurs when the boss is constructed of carboloy. The central rotating member or "anvil" is again a flat surface. The various opposing carboloy surfaces are fashioned on the ends of cylindrical blocks ¾ inch in diameter and $\frac{9}{16}$ inch long, given external support by being forced into hardened steel rings 2.5 inches in diameter.

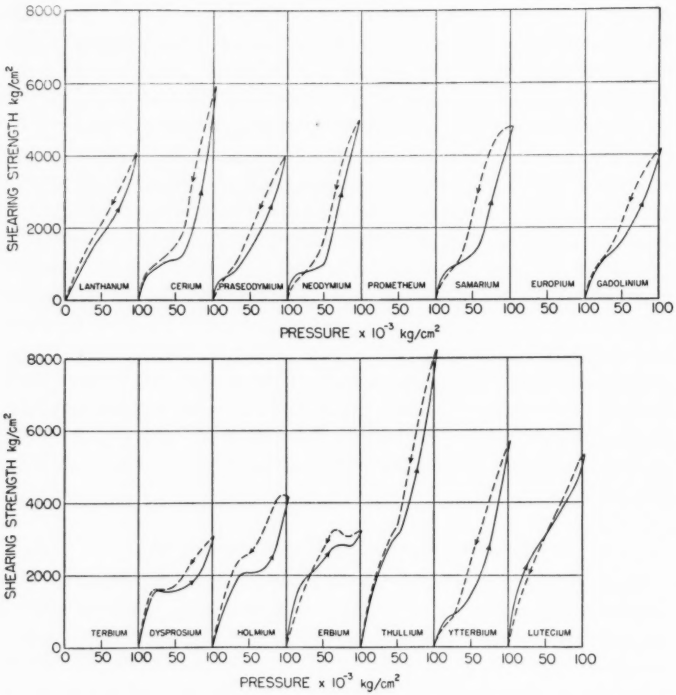

Figure 2. Shearing strength of twelve rare earth metals as a function of pressure to 100,000 kg/cm².

Graphical presentation of the results appears preferable to numerical tabulation. In Figure 2 the shearing strength in kg/cm² is plotted as a function of hydrostatic pressure up to 100,000 kg/cm² for the twelve rare earth metals now available, with blank spaces for the three missing metals, in order the better to show the sequence. The difference between increasing and decreasing pressure shown in all the curves is probably mostly due to irreversible changes in the distribution of the shearing charges on the shearing faces, although there are doubtless cases where part of the difference is due to hysteresis in internal changes in the sheared metal.

The curves of Figure 2 all show anomalies of one sort or another, but nevertheless there is a general family likeness between all the curves. This family likeness is a tendency to a point of inflection near the middle of the pressure range, which sometimes becomes so accentuated as to result in a maximum and minimum, followed toward the end of the range by an upturn with accelerated upward curvature. There are sequences of regular progression of the anomaly, as in the sequence dysprosium, holmium, erbium. There is no apparent close correlation between the anomalies of the shearing curves and the anomalies already found in compression or electrical resistance. Thus the two largest anomalies of resistance in the series, that of cerium at its electronic transition at 12,000 and of ytterbium at its maximum near 60,000, are not reflected in any special local feature of the shearing curves. This agrees with all former experience with these curves, namely that although anomalous features of volume or resistance may be reflected in the shearing curve, there is no necessity for it. If there is a phase change accompanied by a drastic change in lattice type, as presumptively in the cases of bismuth and tellurium for example, then there may also be drastic anomalies in the shearing curve. On the other hand, there are many instances of first order phase transitions in which the accompanying disturbance of the shearing curve is only slight. It seems evident that the shearing curves are giving witness of other features in the mechanism of the solid than merely those which come to light in volume or resistance phenomena. Almost certainly one of the most important of these is transitions which occur only with the cooperation of intense shearing forces in addition to a mean hydrostatic pressure. Theoretically such transitions should occur, but experimentally it may be a matter of considerable difficulty to establish them. One such shearing transition that has been well established experimentally is in lithium.[5]

All the curves of Figure 2 agree in a rapid upturn at the highest pressures. This is not peculiar to these rare earth metals, but is true of nearly all the other metals which have been investigated in the carboloy apparatus up to 100,000 but not yet published. Such an upturn is entirely contrary to what would be expected from the plastic behavior of metals in the range of ordinary stresses. Here the plastic strength is a constant independent of normal

stress across the planes of slip. This means that the shearing curve should approach a horizontal asymptote at high pressures. The fact that it does not is evidence that at high pressures there is a drastic modification in the mechanism of slip. Ordinarily, slip is accomplished with the cooperation of the "dislocations." It does not seem unplausible that at high pressures these dislocations should be squeezed shut or otherwise made incapable of functioning. I have already briefly discussed this matter in the commemorative volume for v. Mises.

Summary and Discussion

It is obvious in the first place that there is an unusual constellation of anomalies at high pressures in the rare earth metals, all but samarium of the twelve now measured exhibiting an anomaly of some kind. It will pay to describe together here the various anomalies of volume and resistance; the anomalies of shearing strength have already been sufficiently exhibited in Figure 2.

Lanthanum shows a discontinuity in volume at 23,700 kg/cm^2, presumably an ordinary first order transition. Its resistance shows a downward cusp between 25,000 and 30,000, presumably due to the same transition. The properties of this metal, and in particular the sharpness of the breaks, are unusually sensitive to perfection of annealing and freedom from cold work. Cerium shows a very large downward break in volume and also in resistance between 7,000 and 12,000. Below the break, resistance increases with rising pressure. It is known from work at the Institute of Metals at Chicago[6] that the transition is accompanied by no change in lattice type; the transition is therefore presumably electronic, within the atom. Beyond the transition the resistance of cerium decreases to a minimum near 80,000, beyond which it increases with a perceptible cusp at 91,000.

The established anomalies of the remaining metals are, with one exception, in the resistance; the volumes up to 40,000, which is as far as the measurements were pushed except for the first four, being smooth. The resistance of praseodymium passes through a flat minimum near 20,000, followed by a sharp downward cusp at 51,000, with a second minimum between 80,000 and 90,000. The resistance of neodymium passes through a flat minimum near 65,000. Gadolinium shows an irreversible decrease of both volume

and resistance near 20,000 on the initial application of pressure. The metal thus irreversibly produced shows no further anomalies. Dysprosium shows a pronounced downward cusp in the resistance between 70,000 and 80,000. Holmium has one or possibly two small and somewhat obscure anomalies of resistance between 20,000 and 40,000, shown in the table as a single downward cusp. Erbium is markedly anomalous, probably due to a very sluggish first order transition, smeared through the entire region between 20,000 and 100,000, the high pressure phase having a positive coefficient of resistance. Thullium has abnormal downward curvature of resistance above 80,000. The unusually high shearing strength of this metal at the high pressure end of the range should also be mentioned. Ytterbium is strikingly anomalous in several respects, for which the detailed presentation should be consulted. Lutecium shows abnormal downward curvature of resistance up to 30,000, beyond which the behavior is normal.

In addition to the specific anomalies just described a review of all the experimental work leaves the impression of an unusual prevalence of seasoning effects with small and sluggish internal changes, in short, a series of metals in which clean-cut, sharp internal equilibrium is not common.

The temperature coefficient of resistance at atmospheric pressure is anomalous throughout the series, being consistently about half, or less, of the value 1/T to be expected for a normal metal. It seems highly unlikely that this is an effect of impurity.

The densities at atmospheric pressure increase on the whole through the series from 6.15 for lanthanum to 9.75 for lutecium, an increase of 58%. The plot of density against atomic number is close to linear, the largest exceptions, except of course ytterbium, being cerium, which lies 10% high, and thullium, which lies 2% low. The atomic weight increases from 139 to 175 through the series, or by 26%, somewhat half of the increase of density. The increasing weight through the series is therefore accompanied by tightening of the whole electronic structure.

The volume compression decreases through the series, the compression under 40,000 dropping from 0.119 for lanthanum to 0.0760 for lutecium, almost inversely as the densities. This direction of progression is what would be expected from the tightening of the electronic structure, but it is to be noticed that it is the

reverse of the direction of progression in the alkali or the alkali earth metals, for example. A plot of volume compression against atomic number is not as smooth as a plot of density and distinctly not linear, tending toward an asymptote with increasing atomic number. The conspicuous deviations from a smooth plot are: cerium, which lies two fold too high (most but not all of the excess being the effect of the transition); neodymium, lying 5% low; samarium, 12% high; gadolinium, 7% low; and ytterbium, nearly three fold high.

Specific resistance at atmospheric pressure is a still more ragged function of atomic weight than density or compression. To a very rough approximation specific resistance is independent of atomic number; to a rough second approximation it rises unsymmetrically to a flat maximum at an atomic number higher than the mean. Conspicuous exceptions are: gadolinium, 65% too high; dysprosium, 35% too low; erbium, 26% too high; and ytterbium, 2.7 fold too low.

In general, the pressure coefficient of resistance is negative throughout the series, although there are many examples of local ranges of pressure in which the coefficient is positive. The effect of pressure on resistance is, except for the effect on shearing strength, the least linear of the pressure effects. In spite of this, the final effect of 100,000 is in all cases to decrease the resistance, on a rough average to something between 0.8 and 0.9 of the initial value. A conspicuous exception is neodymium, for which the decrease of resistance under pressure is abnormally small, in fact smaller than for any other element, the closest approach being by cobalt. Gadolinium is conspicuous by its large drop of resistance under pressure. In view of the very large internal readjustments which take place in ytterbium it would seem more or less of an accident that its resistance at 100,000, in terms of its initial resistance, is not far out of line. Except for ytterbium, the greatest regularity in the pressure effects on resistance in the series is afforded by the heaviest six members, from dysprosium on, the decrease of resistance under pressure tending to decrease with increasing atomic number.

It would appear that the detailed explanation of all these effects will offer a challenge to theory for some time. It is easy to say that the atomic structure in this series is unusual and to point to

the unoccupied inner shells. It is not unnatural to anticipate that the leading motif in the theoretical explanation will be electronic rearrangements within the shells, but the detailed working out appears to be at present a matter of extreme computational difficulty. A first attack might plausibly be directed toward the extreme anomalies of ytterbium.

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